Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Novel cross-linked chromophores based on Diels-Alder reaction or Huisgen reaction

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1. Materials and instruments

The chemicals used in this article are commercially available without further purification unless otherwise specified. The solvents used in the experiments, such as tetrahydrofuran (THF), N, N-dimethylformamide (DMF), and dichloromethane (DCM), were all commercial superdry reagents. TLC analysis with a 0.25 mm thick precoated silica plate allowed spots under UV light.60-100 mesh and 200-300 target silica gel were used for silica column chromatographic separation.

The specific synthesis steps of chromophores WLD1-4 and WLD5 were shown in Fig. 2 and Fig. S1. Their intermediates and the characterization data of mass spectrum, hydrogen spectrum and carbon spectrum are shown in the supporting information.^{1}H-NMR and ^{13}C-NMR spectra were obtained by an Advance Bruker 400M (400 MHz) NMR spectrometer (tetramethylsilane was used as an internal reference). Mass spectra were obtained on a MALDITOF (matrix-assisted laser desorption/flight ionization). BIFLEXIII (Broker Inc.) spectrometer. UV-Vis spectra were performed on a Cary 5000 spectrometer. TGA was determined by TA5000-2950T. TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 °C min^{-1}, under nitrogen protection. Glass-transition temperature (T$_g$) was measured by differential scanning calorimetry (DSC) with a heating rate of 10 °C min^{-1} under the protection of nitrogen.

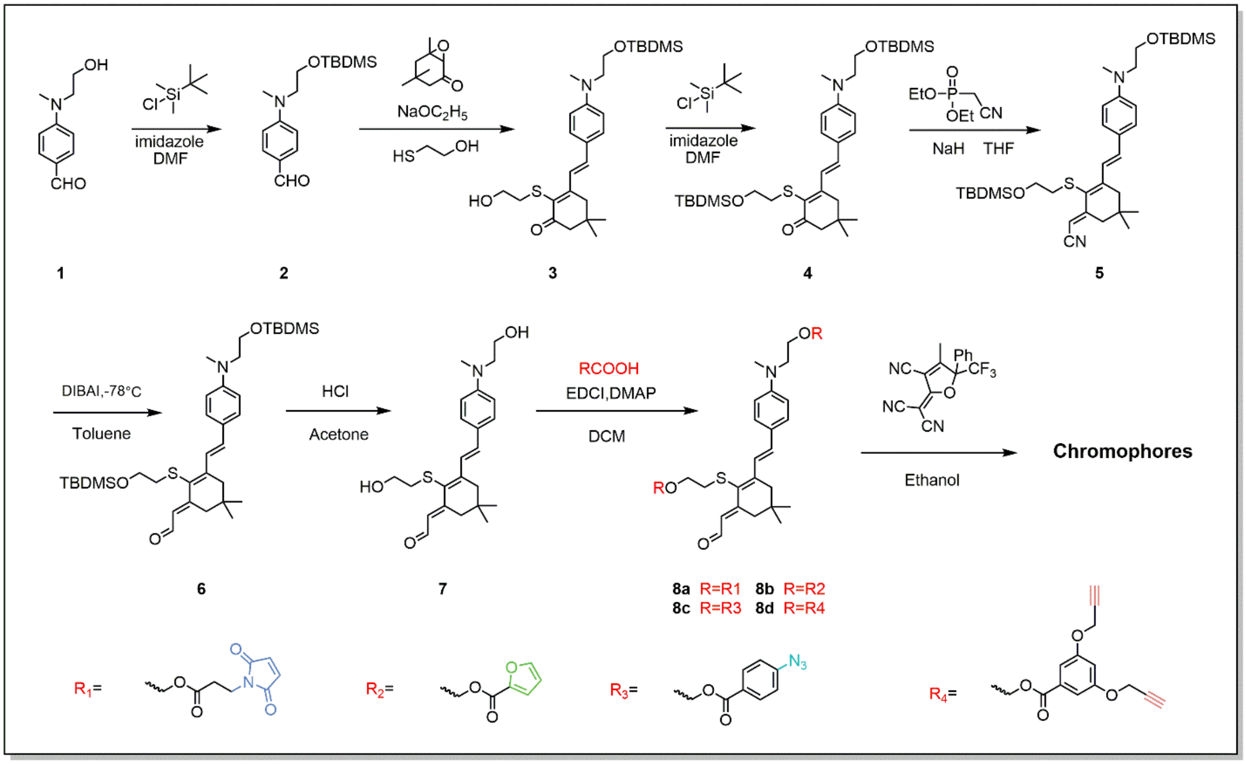


Fig. S1 Synthetic routes for chromophores WLD1-4

2. NMR picture

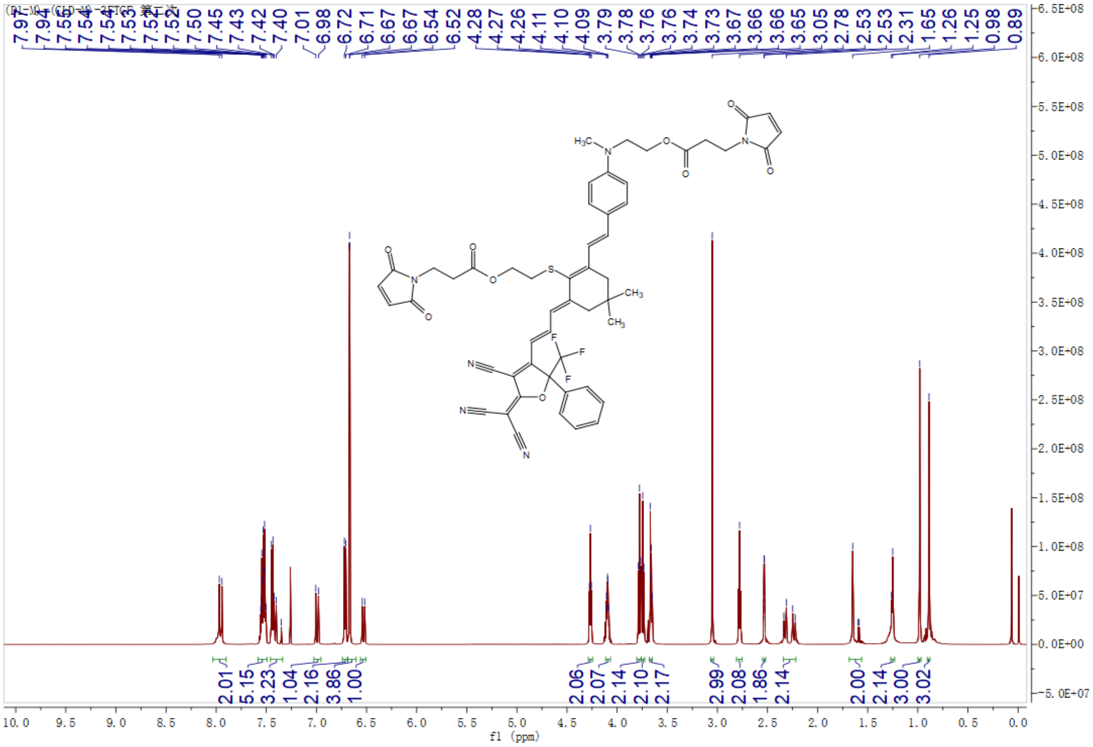


Fig. S2 ^{1}H-NMR spectrum of WLD1

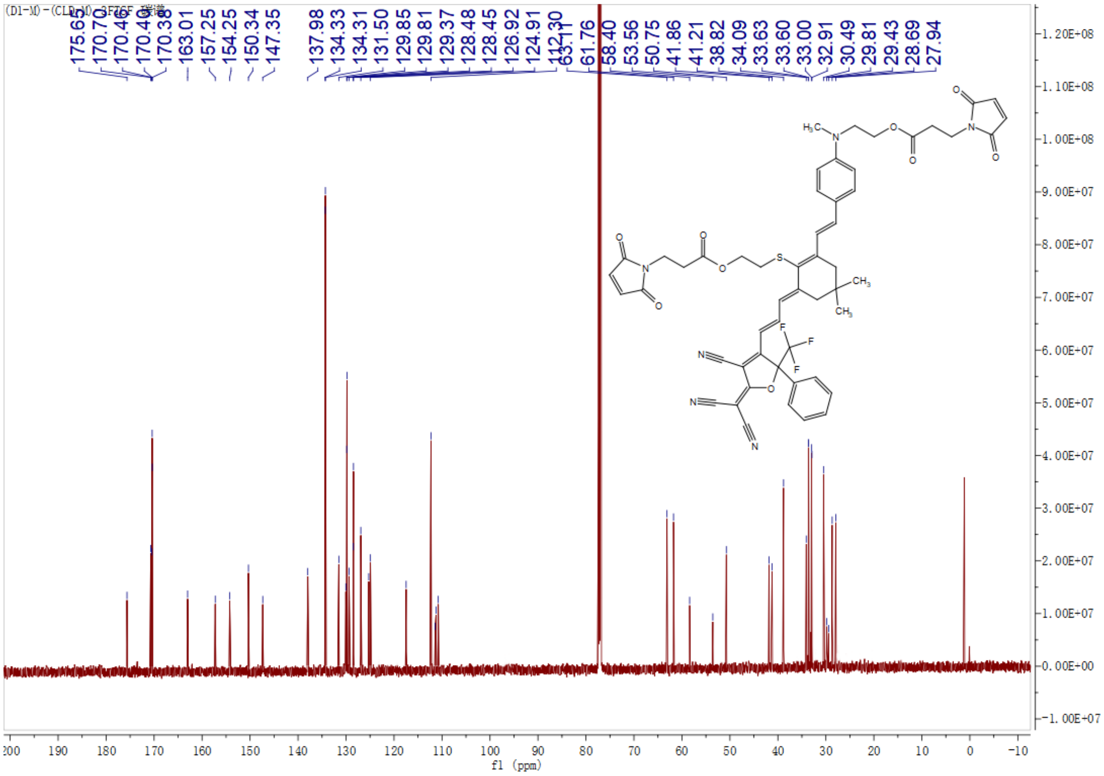


Fig. S3 ^{13}C-NMR spectrum of WLD1

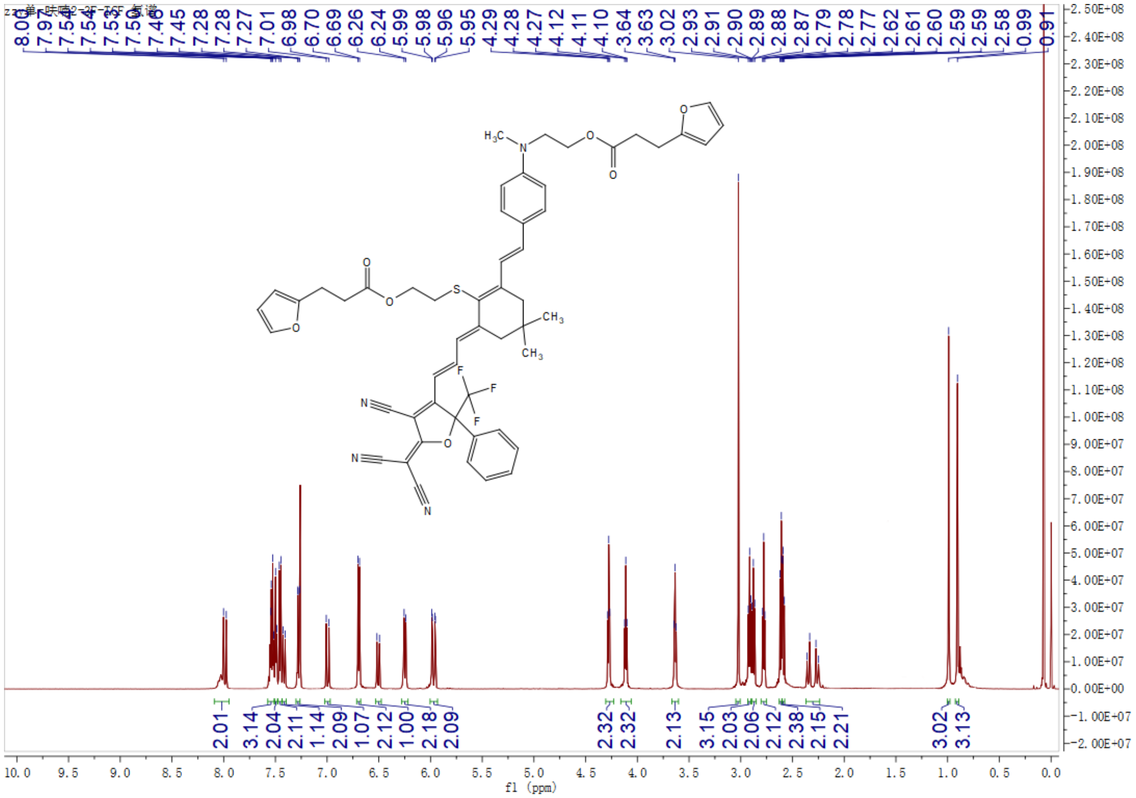


Fig. S4 ^{1}H-NMR spectrum of WLD2

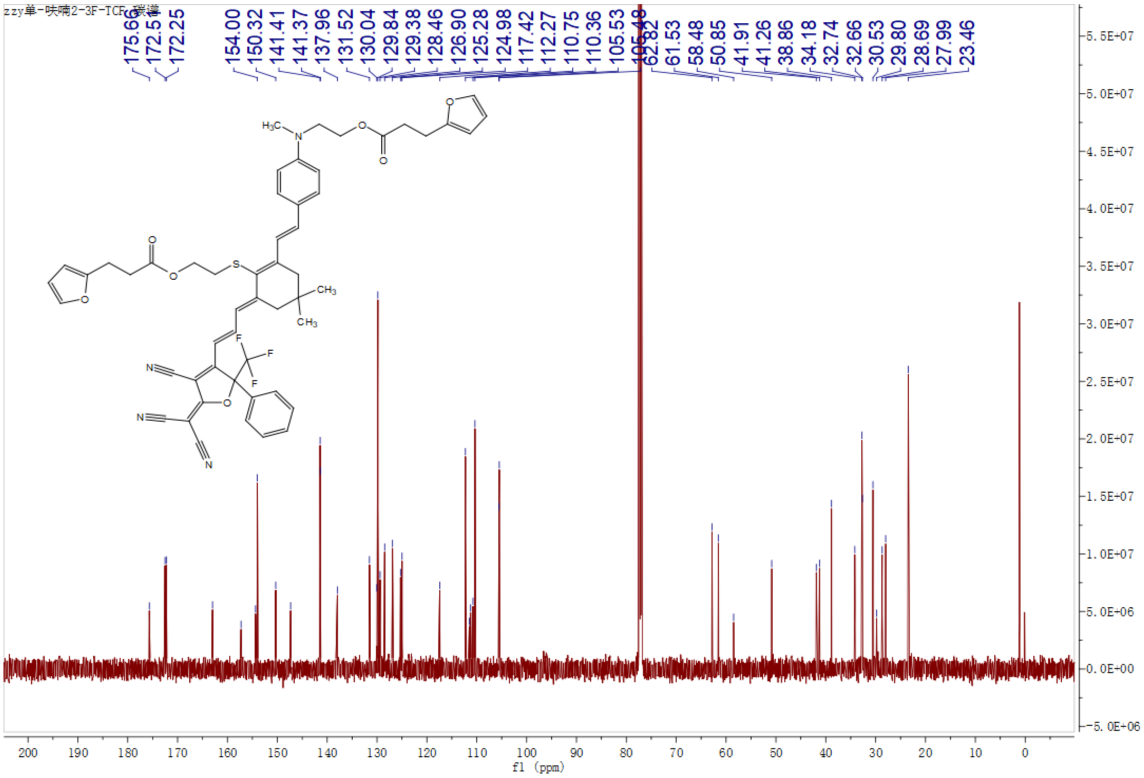


Fig. S5 ^{13}C-NMR spectrum of WLD2

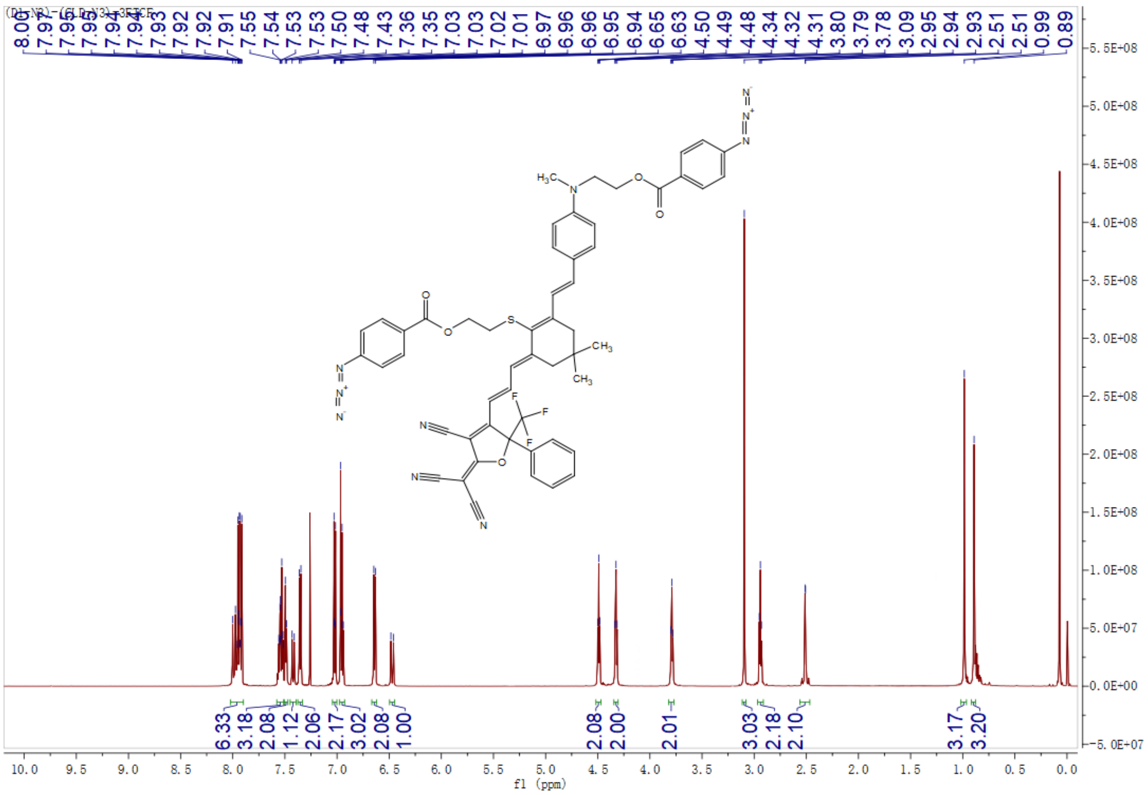


Fig. S6 ^{1}H-NMR spectrum of WLD3

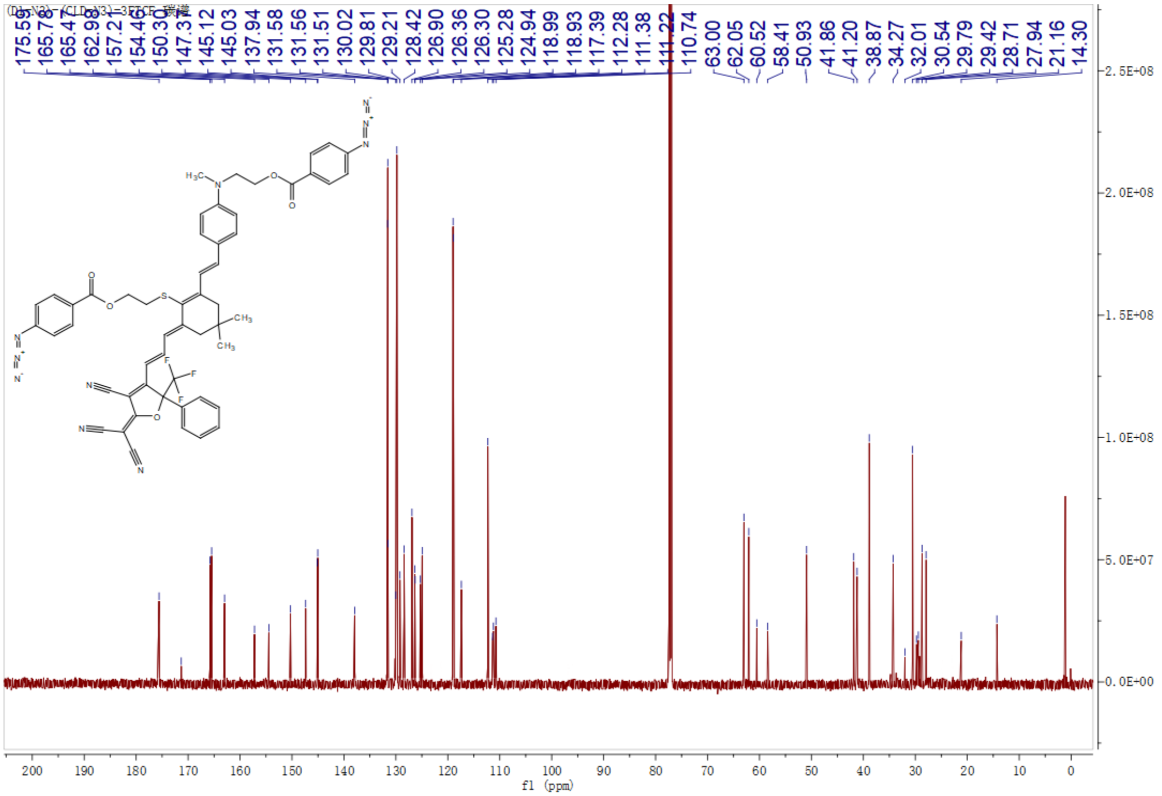


Fig. S7 ^{13}C-NMR spectrum of WLD3

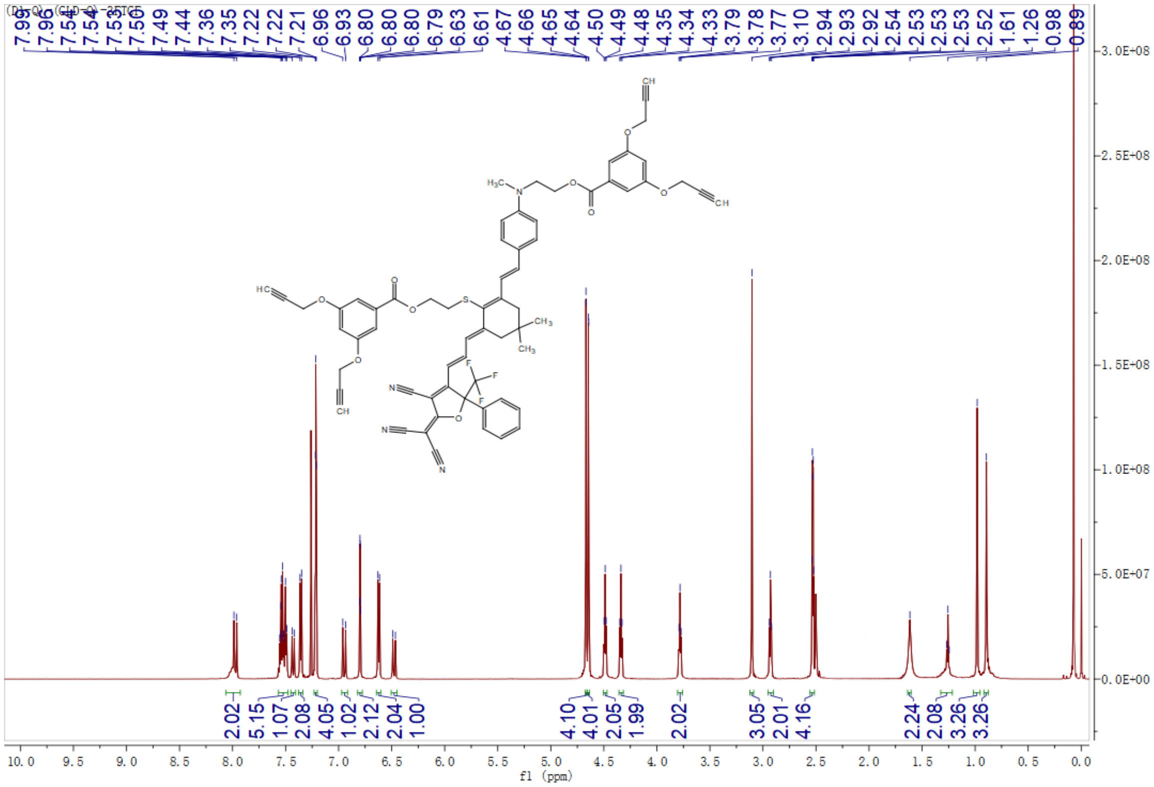


Fig. S8 ^{1}H-NMR spectrum of WLD4

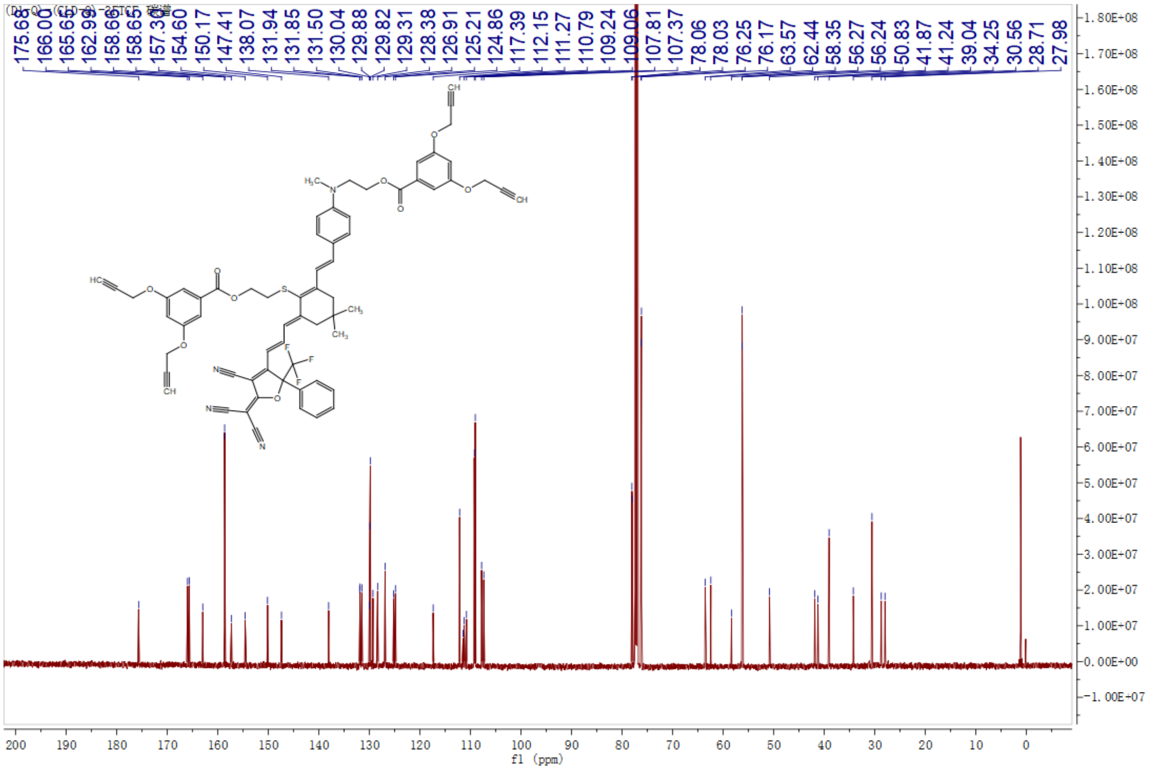


Fig. S9 ^{13}C-NMR spectrum of WLD4

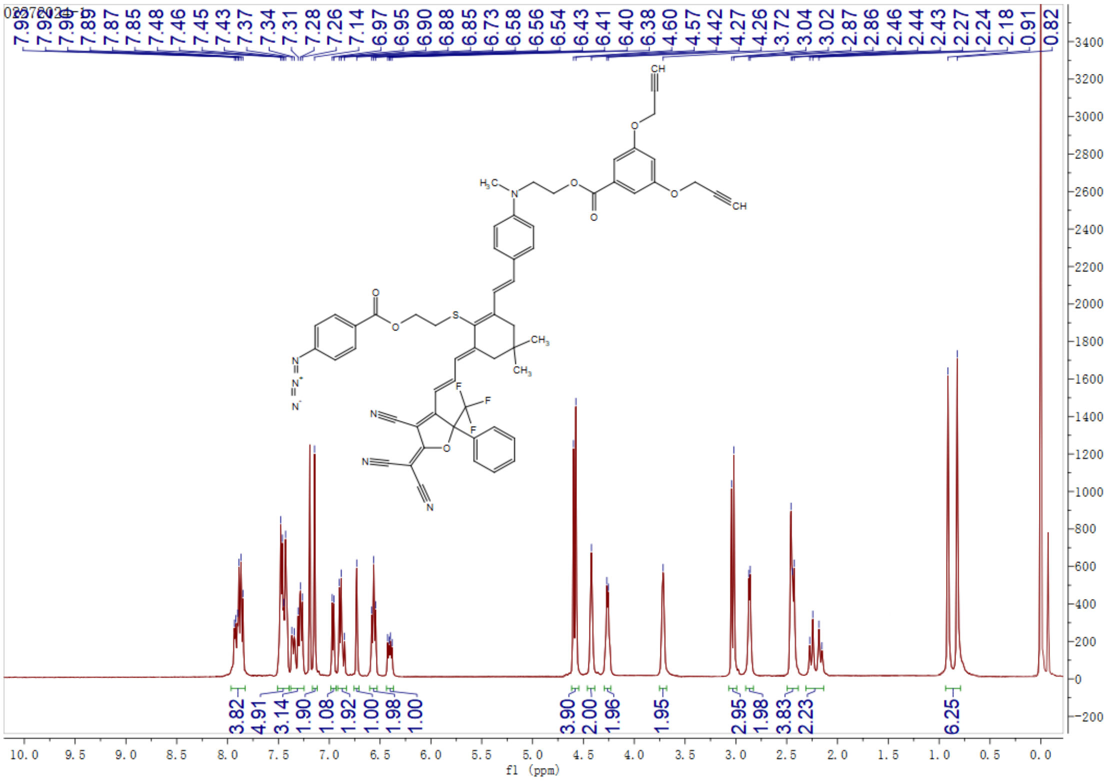


Fig. S10 ^{1}H-NMR spectrum of WLD5

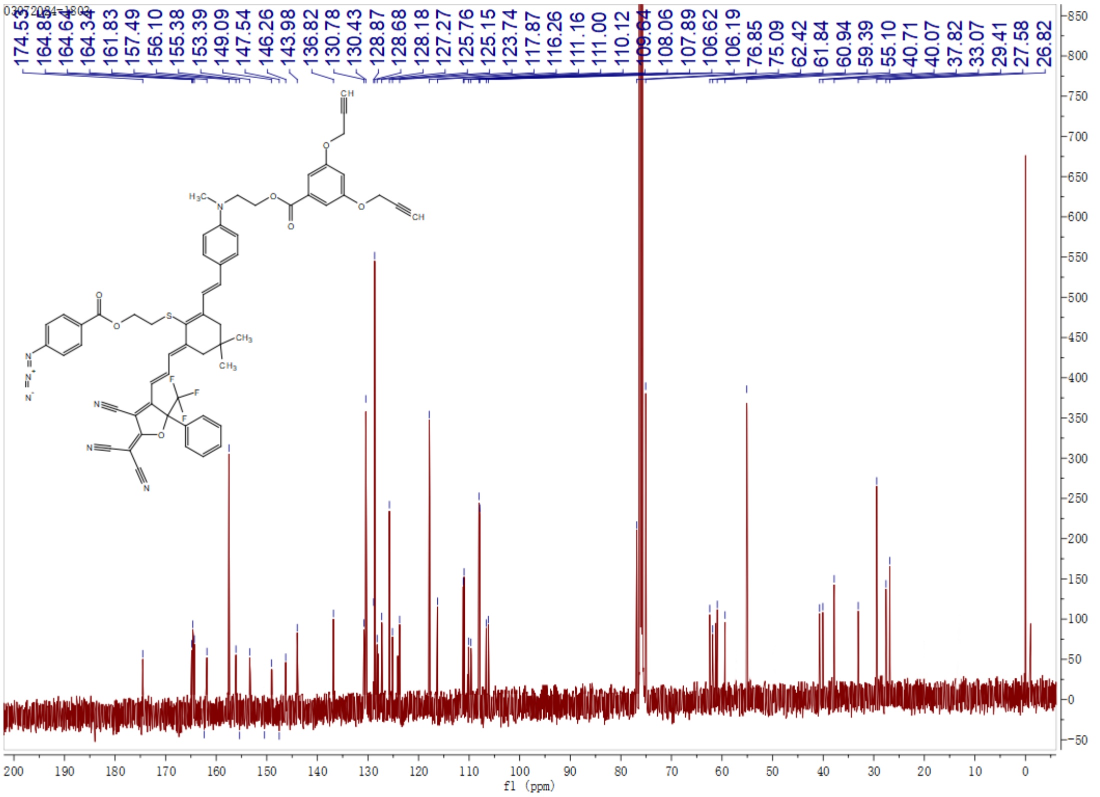


Fig. S11 ^{13}C-NMR spectrum of WLD5

3. UV−vis−NIR Absorption Spectroscopy

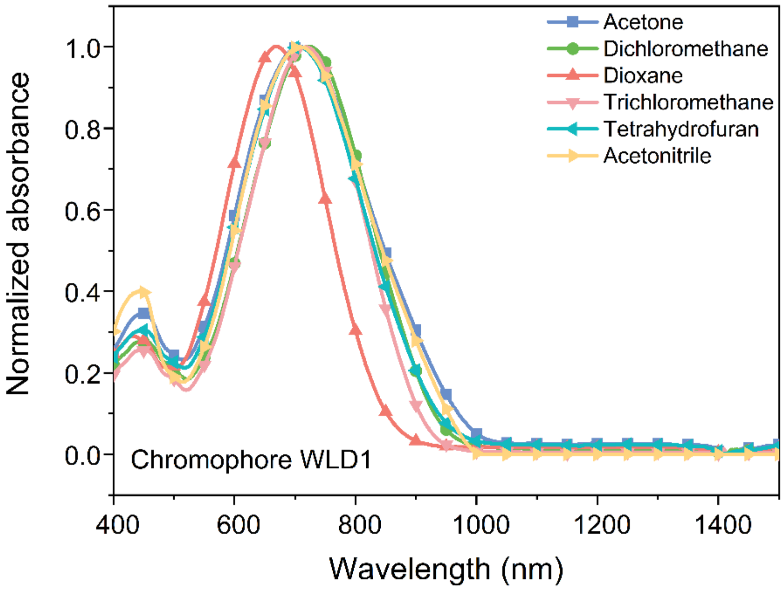


Fig. S12 Normalized UV−vis−NIR absorption spectra of chromophore WLD1 in six aprotic solvents

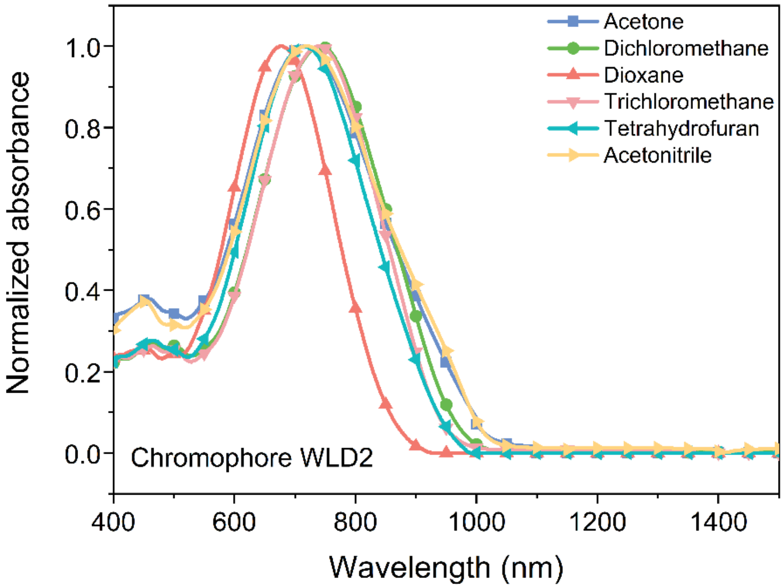


Fig. S13 Normalized UV−vis−NIR absorption spectra of chromophore WLD2 in six aprotic solvents

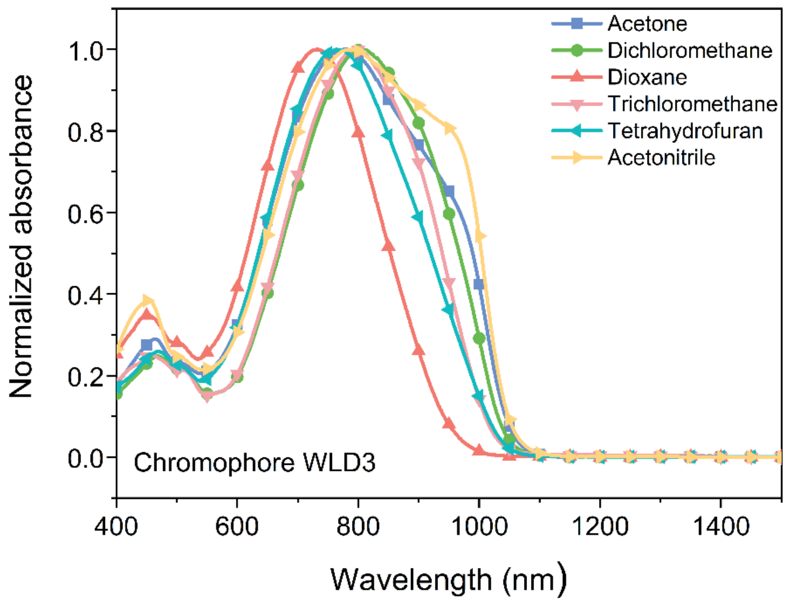


Fig. S14 Normalized UV–vis–NIR absorption spectra of chromophore WLD3 in six aprotic solvents

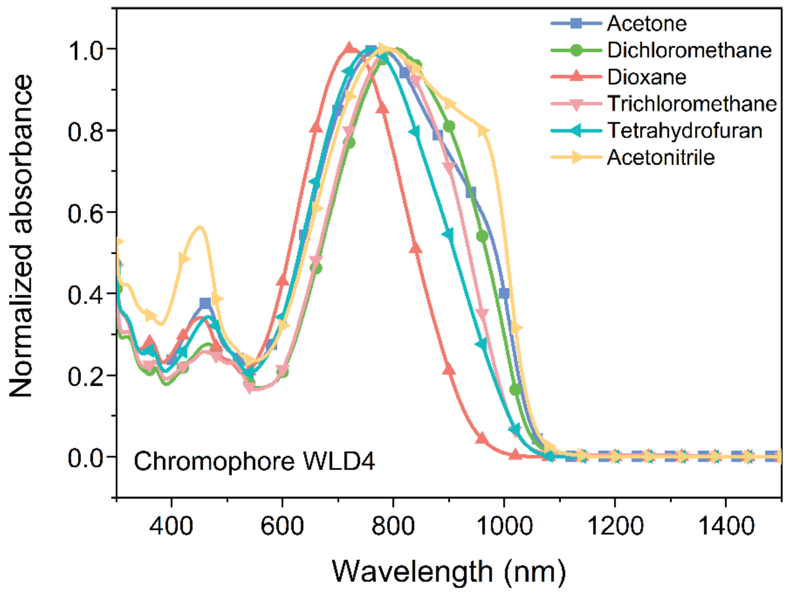


Fig. S15 Normalized UV–vis–NIR absorption spectra of chromophore WLD4 in six aprotic solvents

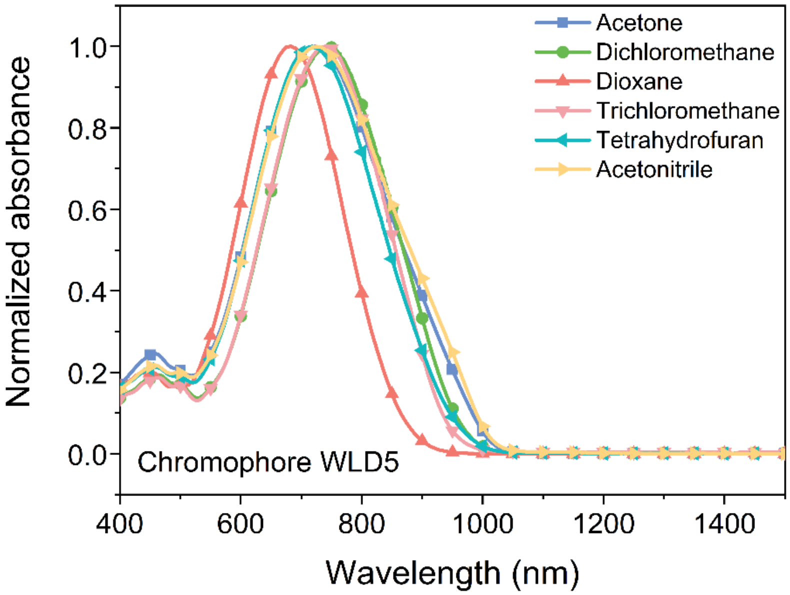


Fig. S16 Normalized UV−vis−NIR absorption spectra of chromophore WLD5 in six aprotic solvents

4. Differential Scanning Calorimetry testing

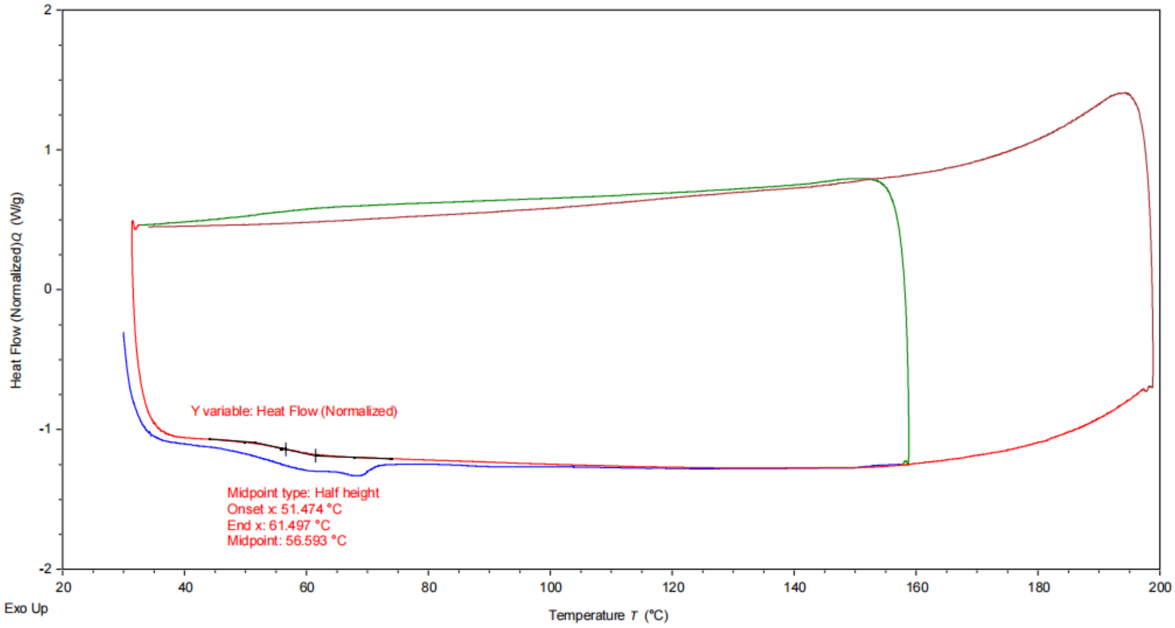


Fig. S17 DSC curves for crosslinking chromophore WLD1

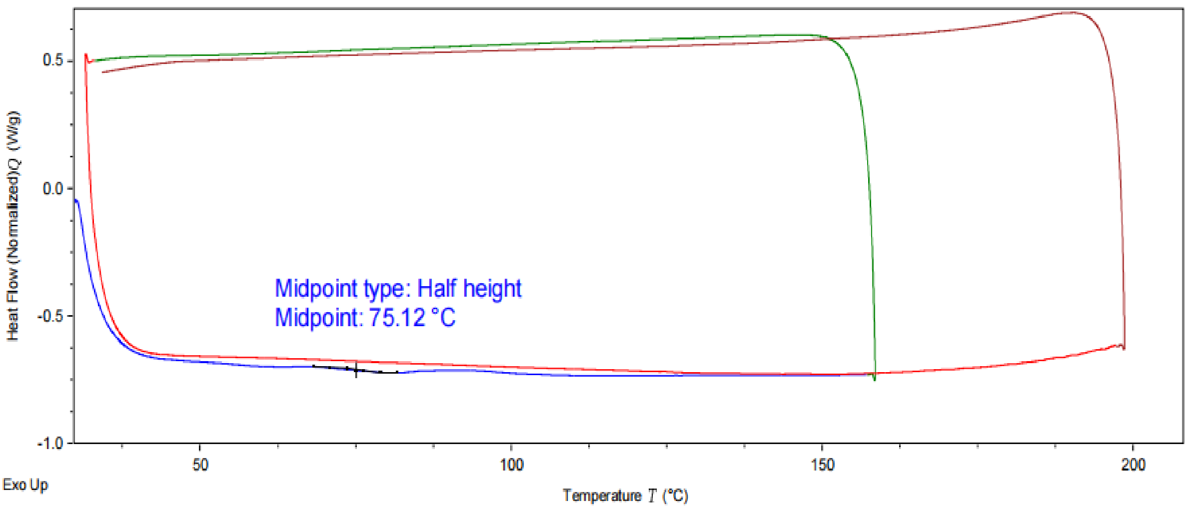


Fig. S18 DSC curves for crosslinking chromophore WLD2

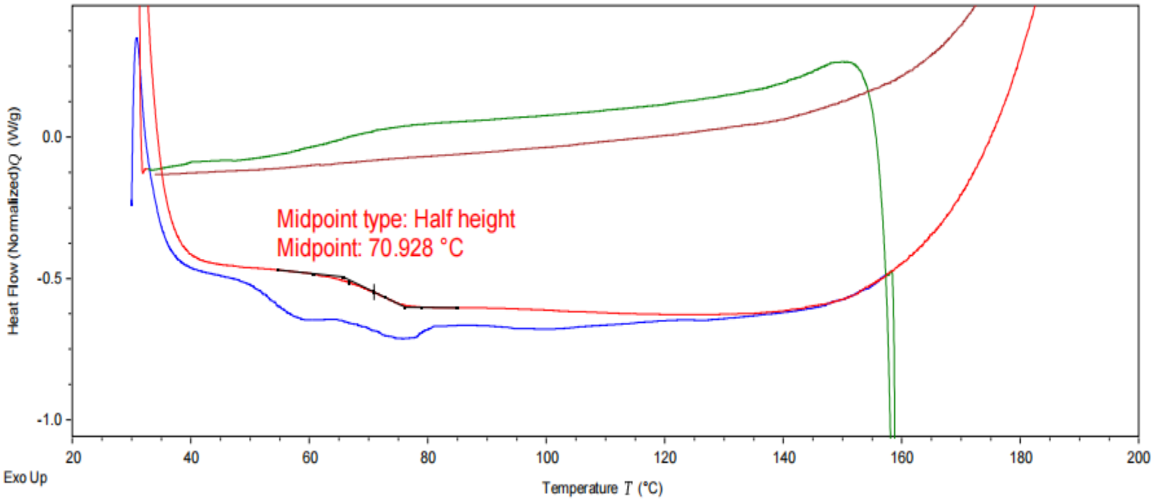


Fig. S19 DSC curves for crosslinking chromophore WLD3

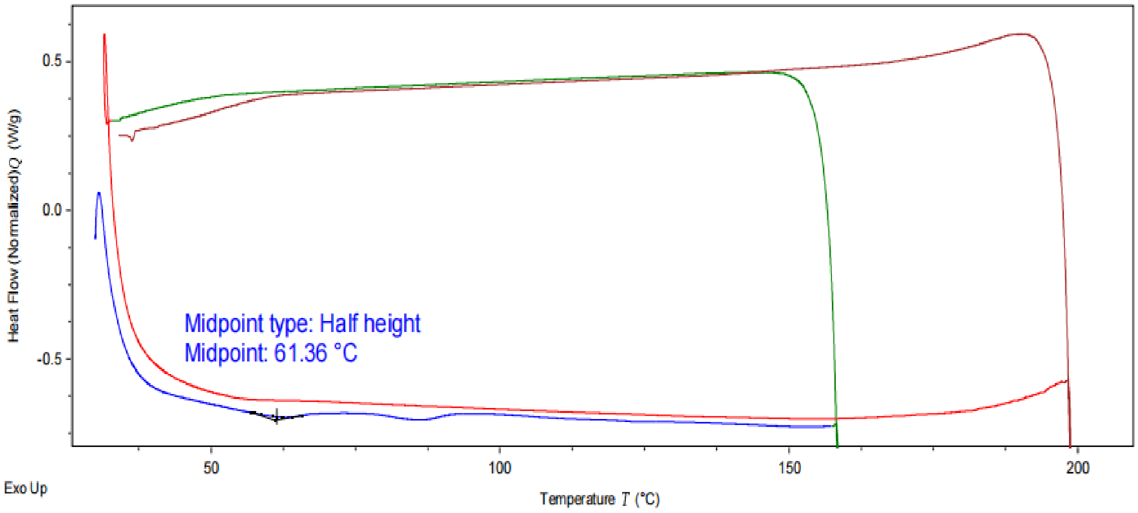


Fig. S20 DSC curves for crosslinking chromophore WLD4

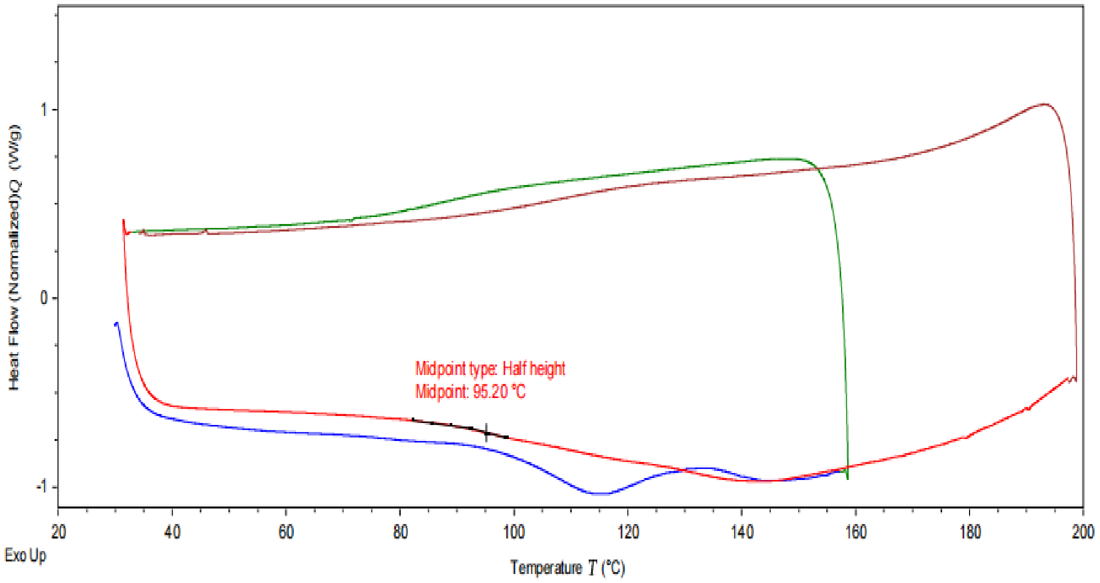


Fig. S21 DSC curves for crosslinking chromophores WLD1/2 before crosslinking

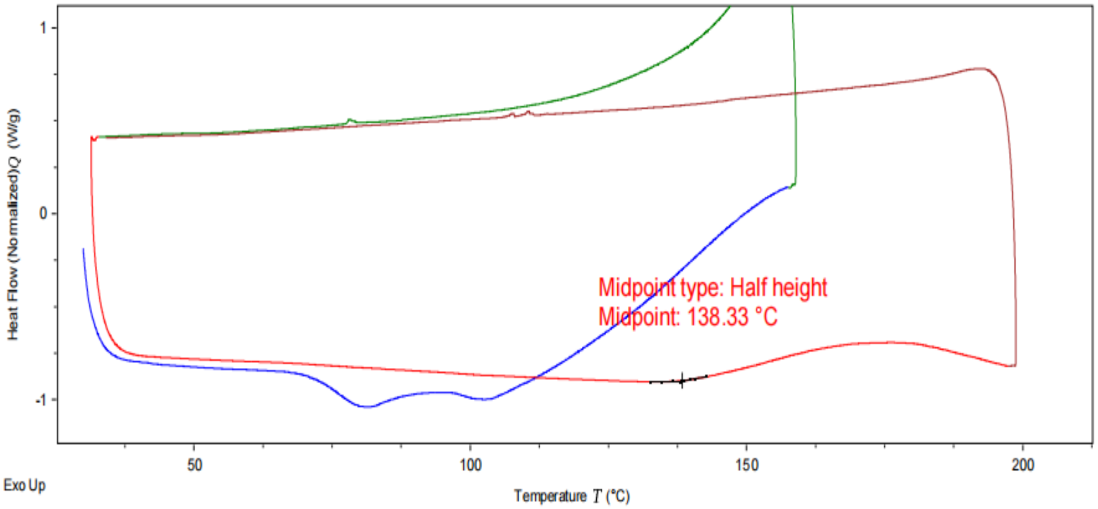


Fig. S22 DSC curves for crosslinking chromophores WLD1/2 after crosslinking

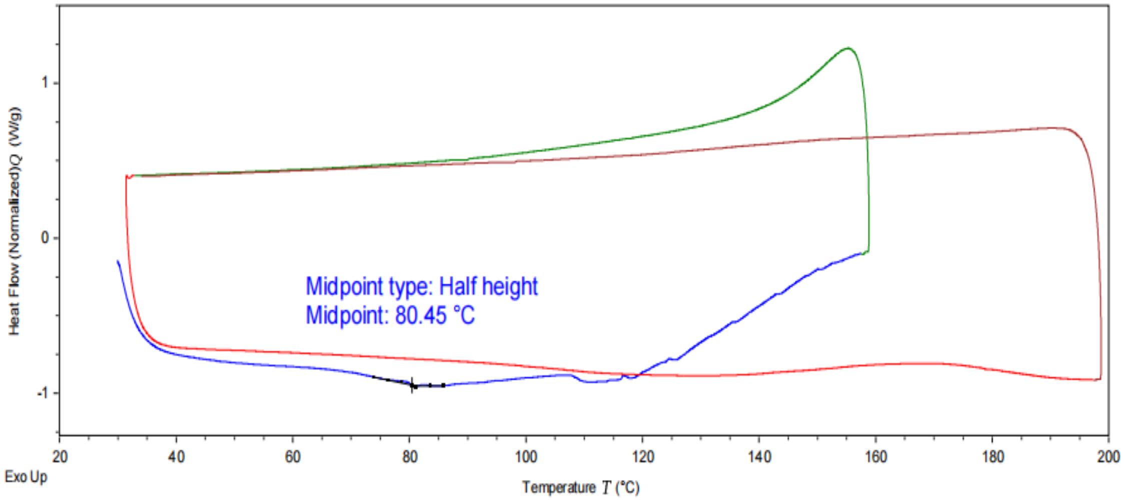


Fig. S23 DSC curves for crosslinking chromophores WLD3/4 before crosslinking

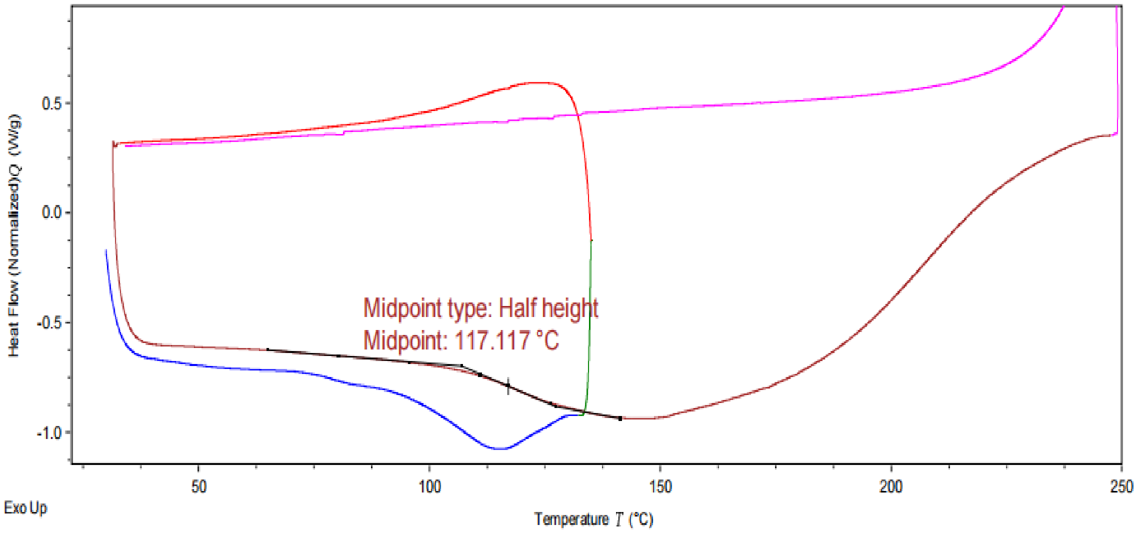


Fig. S24 DSC curves for crosslinking chromophores WLD3/4 after crosslinking

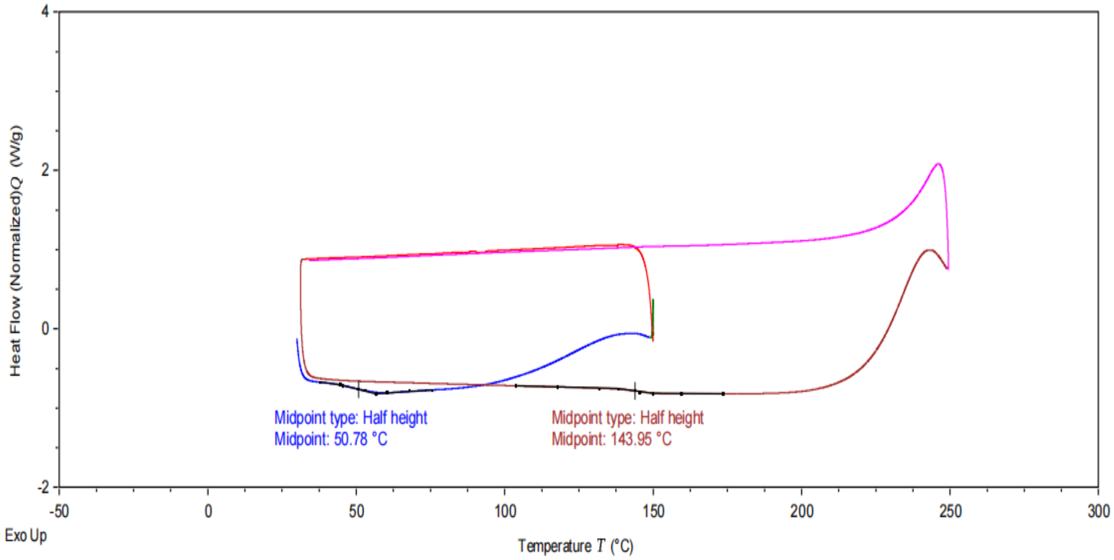


Fig. S25 DSC curves for crosslinking chromophores WLD5 before and after crosslinking

5. DFT Calculations

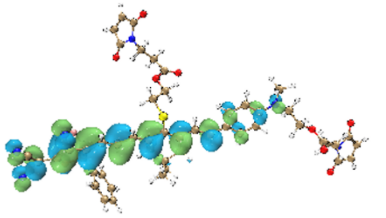
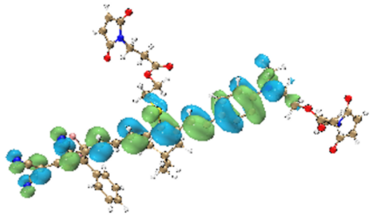
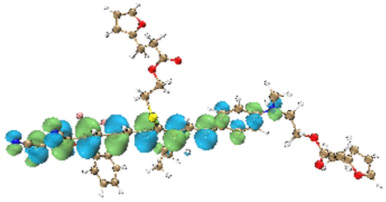
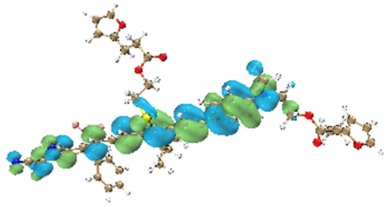
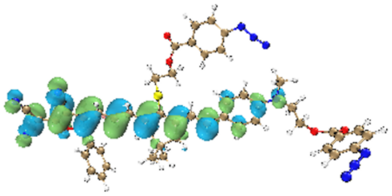
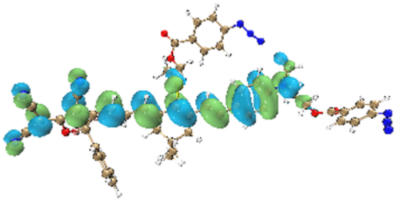
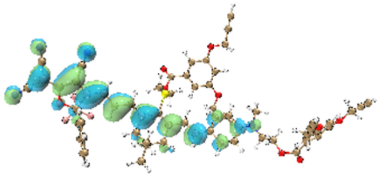
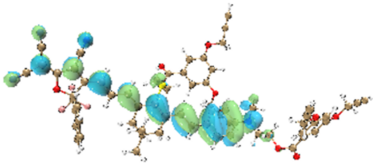
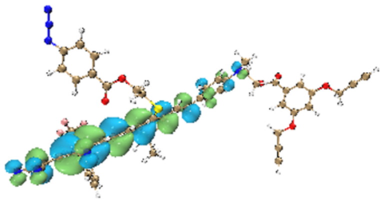
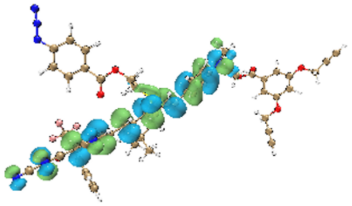
	HOMO	LOMO
WLD1		
WLD2		
WLD3		
WLD4		
WLD5		

Fig. S26 Frontier molecular orbitals HOMO and LUMO of chromophores WLD1-5

6. Device Fabrication and Testing.

1)Materials and Preparation:

1,1,2-Trichloroethane (TCE) was dried over $CaCl_2$ for several days and distilled under vacuum before use. ITO/glass slides (Thin Film Devices, Inc.; 45 nm thickness, ⩽100 Ω/sq resistivity, ⩾85% transmission at 1300–1500 nm) were used as substrates.

2)Film Fabrication:

Solutions of 8–10% w/w electro-optic (EO) material in TCE were sonicated for 15 min, filtered (0.2 µm PTFE), and spin-cast onto ITO/glass (with or without BCB barrier layers) using a three-step process: 500 rpm (5 s), 850 rpm (30 s), and 1500 rpm (30 s). Films were dried either overnight at room temperature under vacuum or at 65°C for 6–12 hr, yielding 1–2 µm thickness (measured by optical profilometry). Patterned Au electrodes were sputter-coated through a shadow mask to complete the device.

3)Poling and Characterization:

For non-crosslinked EO films, electric field poling involved heating to T_g under an applied field, holding for ~10 min, cooling, and removing the field. The electro-optic coefficient (r_{33}) was measured at 1310 nm (Teng–Man technique[1]; with errors calculated as described previously. To prevent cracking during high-temperature crosslinking, a step-poling method [2] was employed (details in main text) for the crosslinked films.

REFERENCES

1. Y. Shuto and M. Amano, Journal of Applied Physics, 1995, 77, 4632-4638.
2. H. Xu, F. Liu, D. L. Elder, L. E. Johnson, Y. de Coene, K. Clays, B. H. Robinson and L. R. Dalton, Chemistry of Materials, 2020, 32, 1408-1421.